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Theoretical Study of Oxidative Addition to Platinum Metal Complexes. IV. Thermodynamic Substrate and Regioselectivities of 16-Electron Planar Complexes of Rhodium(I) and Palladium(II) and Cyclopentadienyl Complexes of Platinum(II) and Iridium(I) in Reactions with Small Alkanes

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Abstract

Nonempirical MO calculations by the GAMESS program were used to perform full geometry optimization of products of methane, ethane, and propane oxidative addition to the square-planar complexes RhCl(PH3)3 and PdCl2(PH3)2 and to the cyclopentadienyl derivatives CpMCl (M = Pt, Ir-) and CpIr(PH3). The most stable conformers formed by rotation about the metal-alkyl bond were determined. The energies of the reactions were calculated with allowance for electron correlation by the MP2 and B3LYP methods using the GAUSSIAN 94 package. Substrate and regioselectivities of the metal complexes were determined. The "classical" selectivity order i-Pr-H ≫ n-Pr-H ≥ Et-H > Me-H for platinum complexes was shown to correspond to prevailing contribution of electronic factors to the energy of the metal-alkyl bonds, whereas increased energy of steric alkyl-ligand interactions produces partial or complete inversion of this order, resulting in "nonclassical" selectivity. The difference in the MP2 and B3LYP selectivites is explained by the fact that the first method overestimates the electronic contribution to the energy of the metal-alkyl bond.